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QUARTERMASTER RESEARCH & ENGINEERING COMMAND
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RADIATION CHEMISTRY LABORATORY SERIES
RESEARCH REPORT NO. 8

IRRADIATION "FACTOR-DEPENDENCY"

Some Vinyl Monomers:

Dose Rate and other Variables

NOV 6 1962

QUARTERMASTER RESEARCH & ENGINEERING CENTER
PIONEERING RESEARCH DIVISION

JUNE 1961   NATICK, MASSACHUSETTS

FOREWORD

This report, Research Report No. 8, Irradiation "Factor-Dependency," Radiation Chemistry Laboratory Series, deals with the effect of dose rate and other variables on the irradiation-induced polymerization of certain vinyl monomer systems.

Data of Research Report No. 1, Styrene, indicate that factors such as atmosphere, degassing, diluent, dose, dose rate, moisture, and temperature all appear to be important parameters. Atmosphere, dose rate, and temperature were found to be statistically significant, with variations in dose rate being approximately twice as effective as variations in either atmosphere or temperature. With respect to molecular weight, temperature was found to be statistically significant at dose rates of 25,000, 50,000, and 100,000 rads per exposure. The non-additivity of dose was reported.

Research Report No. 2, Some Vinyl Monomers, gave results which indicate that under the experimental conditions employed: (1) polymerization rate is not equal to $kI^{1/2}$, (2) the E-value ("G_e"-value or amount of polymer obtained per unit of radiation energy) decreases with an increase in dose rate, (3) there is a non-additivity of dose, and (4) unless parameters are critically defined, the formulation of reaction rate has no significance.

Research Report No. 3, Styrene with Additives, provided data from which it was concluded for the additives used that: (1) the effect of an additive is a function of dose rate with respect to both molecular weight and conversion to polymer, and may either catalyze or inhibit polymer formation, (2) the molecular weight decreases with an increase in dose rate for all additives used, (3) there appears to be an inverse ratio with respect to conversion and molecular

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weight, and (4) the efficiency of polymerization decreases markedly at the higher dose rates used in these studies.

In Research Report No. 4, Irradiation Cycle, it was concluded that: (1) a cycle of something more than three minutes at 75°C. is the most efficient for the irradiation-induced polymerization of certain vinyl monomers, (2) the better relative efficiency of a time cycle over continuous irradiation decreases with an increase in dose rate, (3) efficiency decreases markedly at the higher dose rates used in these studies, (4) reaction rate formulations, derived under experimental conditions different from those used in this study, are not applicable, and (5) the most desirable time cycle and temperature are functions of the monomer system.

Research Report No. 5, Degassing, presented experimental results from which it was concluded that: (1) degassing may significantly increase the conversion to polymer obtained by the irradiation-induced polymerization of vinyl monomers, and (2) the relative importance of degassing is interdependent on (a) the monomer system, (b) the dose rate, and (c) in certain cases at least, the presence of an inert atmosphere such as argon.

From data on the composite effect of degassing and the irradiation cycle, Research Report No. 6, it was concluded that: (1) with the other parameters used in this study, an irradiation cycle of more than three minutes is required for optimal conversion to polymer at a given dose rate and dose level, (2) both the effect of degassing and the irradiation cycle are dependent to some extent on the monomer system, (3) degassing is more dependent, with respect to its effect, on the monomer system than is the irradiation cycle, and (4) the relative composite effect of degassing and the irradiation cycle decreases in general with an increase in dose rate and total dose.

From the data obtained in a study of multiple parameters for the irradiation-induced polymerization of certain vinyl monomer systems (Research Report No. 7), it was concluded that the effect of: (1) air is dependent on the monomer system, (2) flame-out of the tubes under vacuum before introduction of the monomer is dependent on the chemical entity, (3) degassing once, twice, or three times is dependent on the monomer system, and (4) the combination of flame-out and degassing is also a function of the monomer system.

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Irradiation "Factor-Dependency": Dose Rate

and Other Variables

By Ed. F. Degering, Gerald J. Caldarella, and Flora E. Evans

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A. Introduction

The experimental results presented in this report are taken from a series of studies during the past seven years in which consideration has been given to dose rate in the irradiation-induced polymerization of certain vinyl monomer systems by use of 1.5 and 2 Mev electron accelerators, which were both operated at 2 Mev.

In each of the previous numbers of this series, some studies were reported on dose rate, as may be observed from the foreword. The purpose of this report is to present in compact form some of the implications of dose rate on the irradiation-induced polymerization of vinyl monomers, including interdependency on experimental conditions and operational parameters.

B. Preparation of Samples

The procedure developed by the Radiation Chemistry Laboratory (cf. Research Report No. 4, Section B, page 1, December 1960, and Research Report No. 5, Section B, page 1, January 1961) for the preparation of monomer systems for irradiation with high velocity electrons has been used in general for the studies reported herein. The data for Figures 1 to 7 (pages 2 to 8) were from samples which were subjected
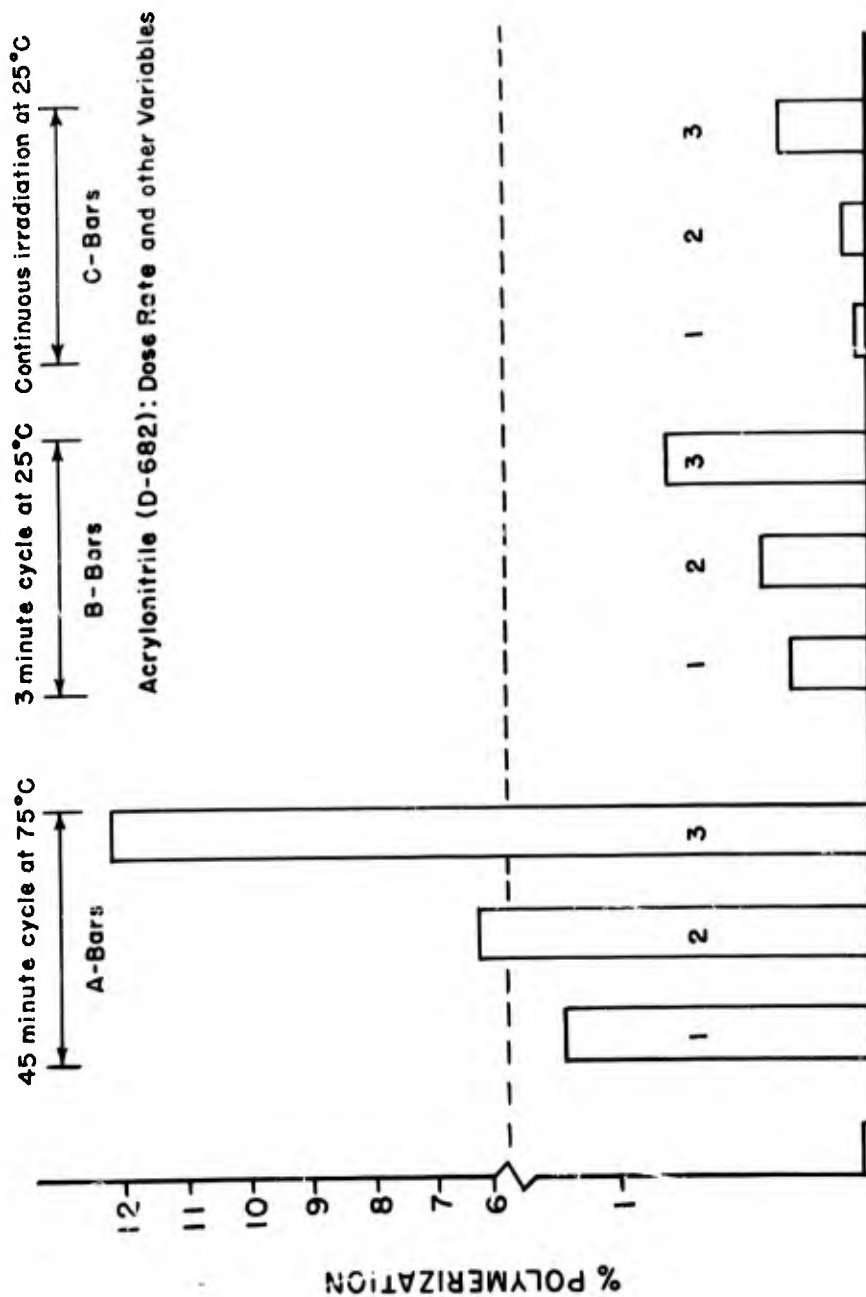
Figure 1. The 1-bars received 1,000 rads per exposure, or 250 rads per second, to a dose of 5,000 rads; the 2-bars received 10,000 rads per exposure, or 2,500 rads per second, to a dose of 50,000 rads; and the 3-bars received 100,000 rads per exposure, or 25,000 rads per second, to a dose of 500,000 rads.

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% POLYMERIZATION

45 minute cycle at 75°C   3 minute cycle at 25°C   Continuous irradiation at 25°C

A-Bars   B-Bars   C-Bars

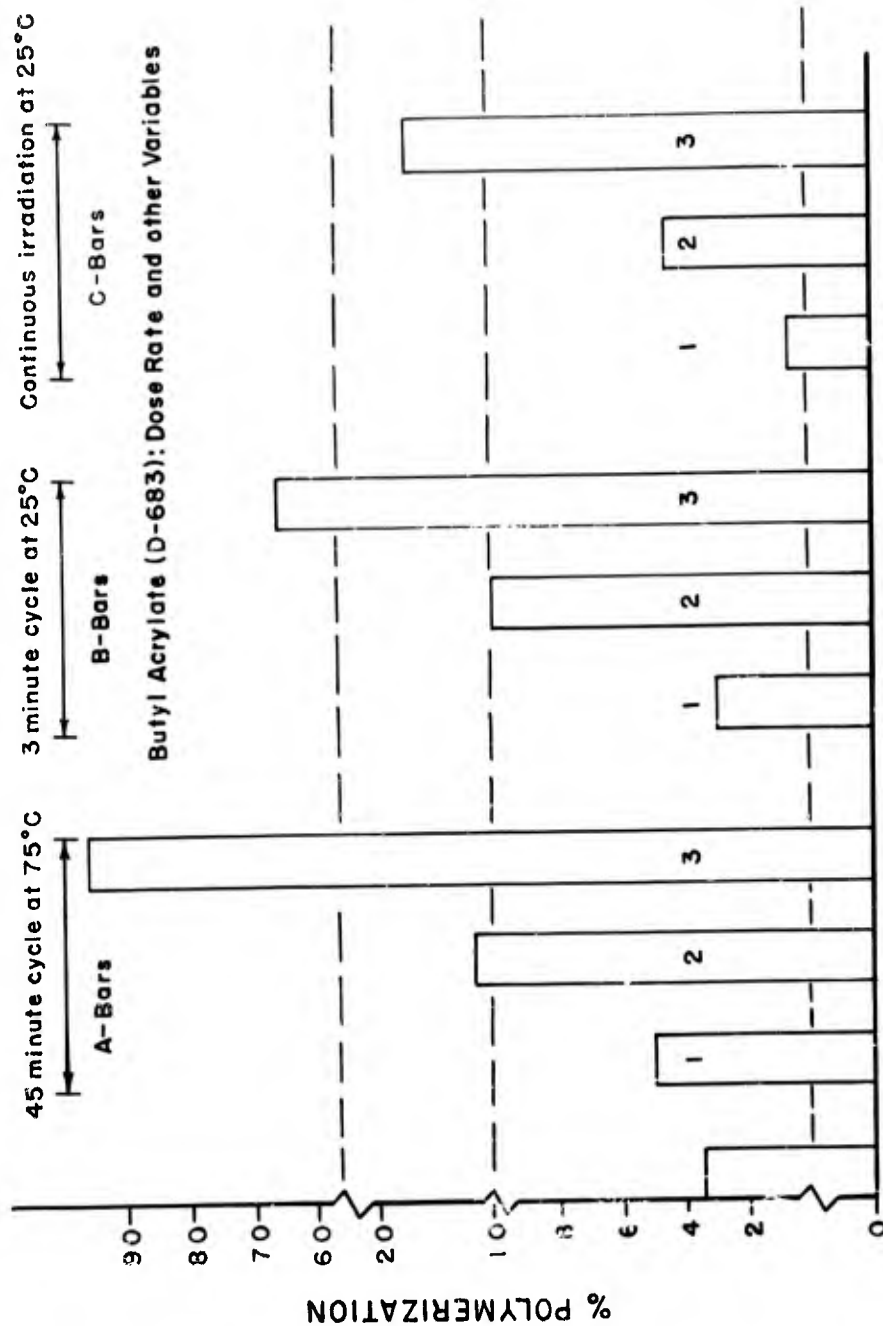Butyl Acrylate (D-683): Dose Rate and other Variables

Figure 2.   The 1-bars received 1,000 rads per exposure, or 250 rads per second, to a dose of only 1,000 rads; the 2-bars received 10,000 rads per exposure, or 2,500 rads per second, to a dose of 50,000 rads; and the 3-bars received 100,000 rads per exposure, or 25,000 rads per second, to a dose of 500,000 rads.
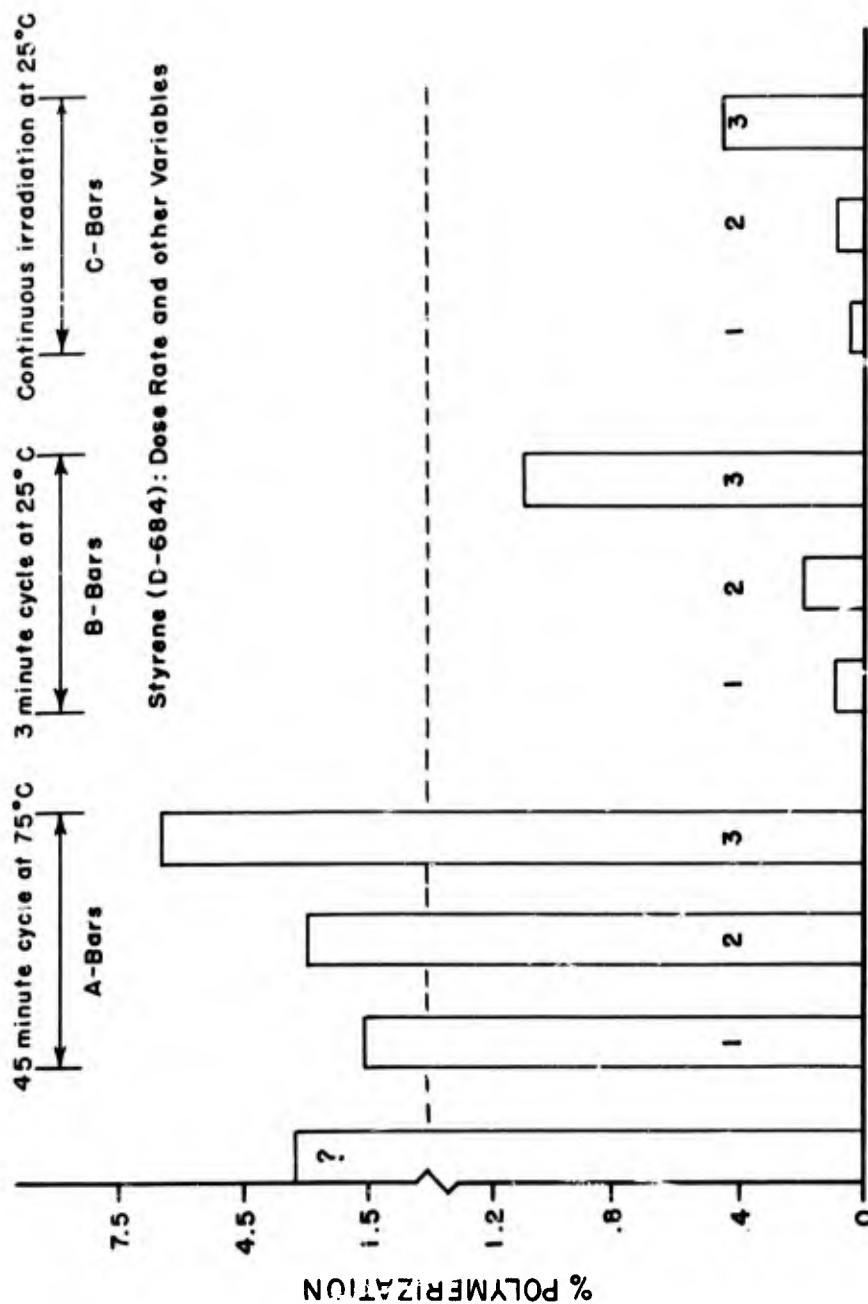
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Figure 3. The 1-bars received 1,000 rads per exposure, or 250 rads per second, to a dose of 5,000 rads; the 2-bars received 10,000 rads per exposure, or 2,500 rads per second, to a dose of 50,000 rads; and the 3-bars received 100,000 rads per exposure, or 25,000 rads per second, to a dose of 500,000 rads.

4

% POLYMERIZATION

45 minute cycle at 75°C   3 minute cycle at 25°C   Continuous irradiation at 25°C

A-Bars   B-Bars   C-Bars
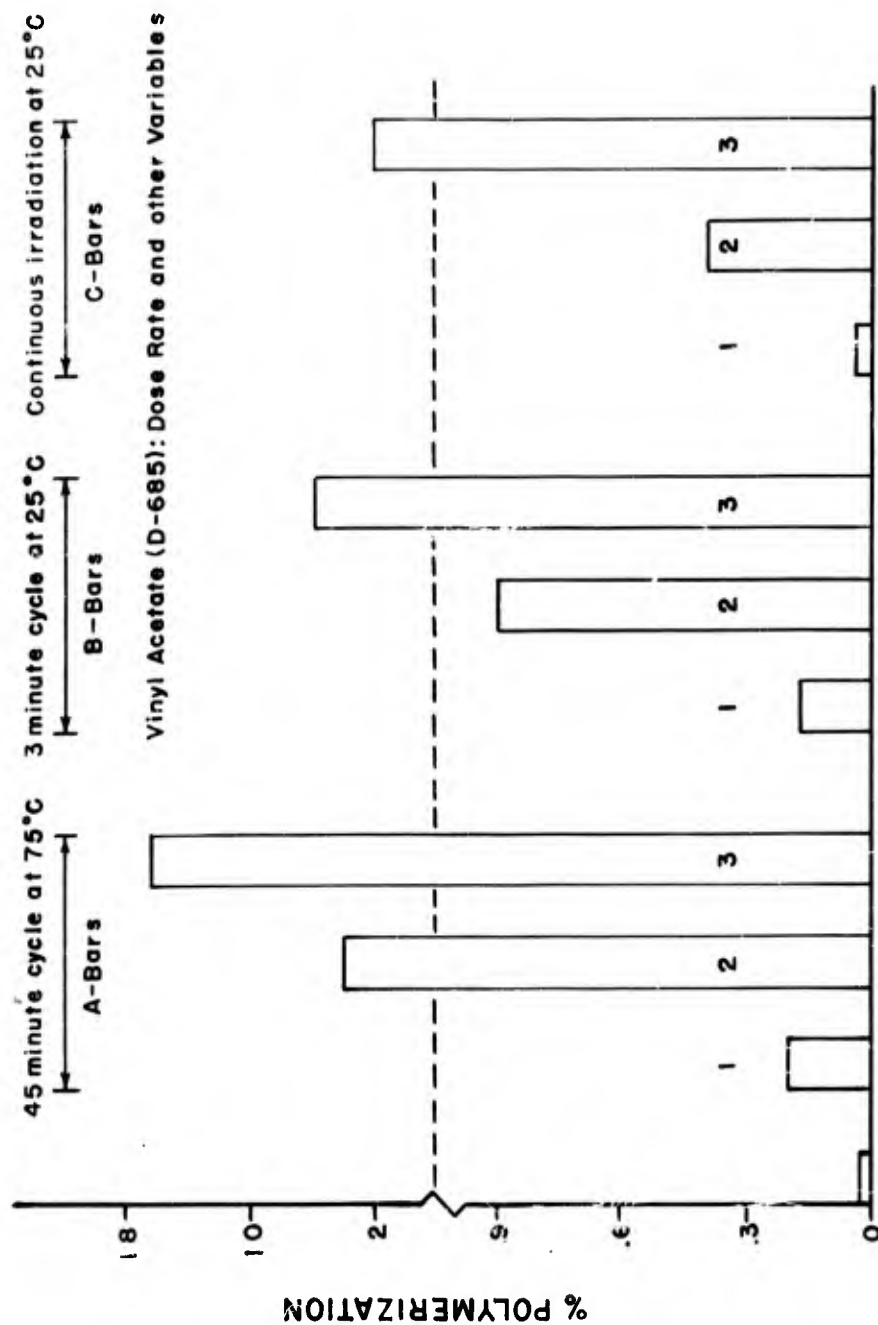
Vinyl Acetate (D-685): Dose Rate and other Variables

Figure 4. The 1-bars received 1,000 rads per exposure, or 250 rads per second, to a dose of 5,000 rads; the 2-bars received 10,000 rads per exposure, or 2,500 rads per second, to a dose of 50,000 rads; and the 3-bars received 100,000 rads per exposure, or 25,000 rads per second, to a dose of 500,000 rads.
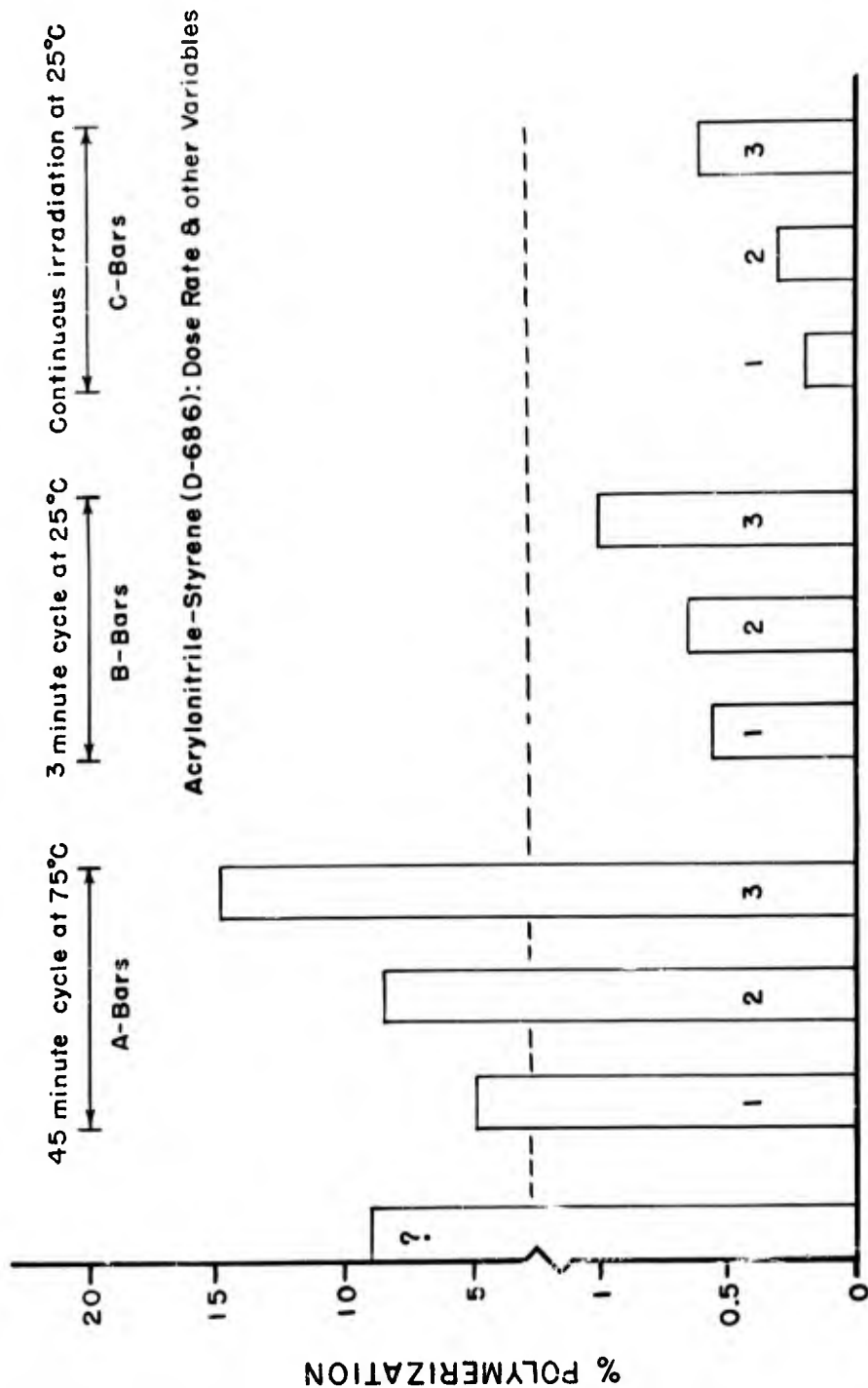
45 minute cycle at 75°C   3 minute cycle at 25°C   Continuous irradiation at 25°C

A-Bars   B-Bars   C-Bars

Acrylonitrile-Styrene (D-686): Dose Rate & other Variables

% POLYMERIZATION

Figure 5. The 1-bars received 1,000 rads per exposure, or 250 rads per second, to a dose of 5,000 rads; the 2-bars received 10,000 rads per exposure, or 2,500 rads per second, to a dose of 50,000 rads; and the 3-bars received 100,000 rads per exposure, or 25,000 rads per second, to a dose of 500,000 rads.
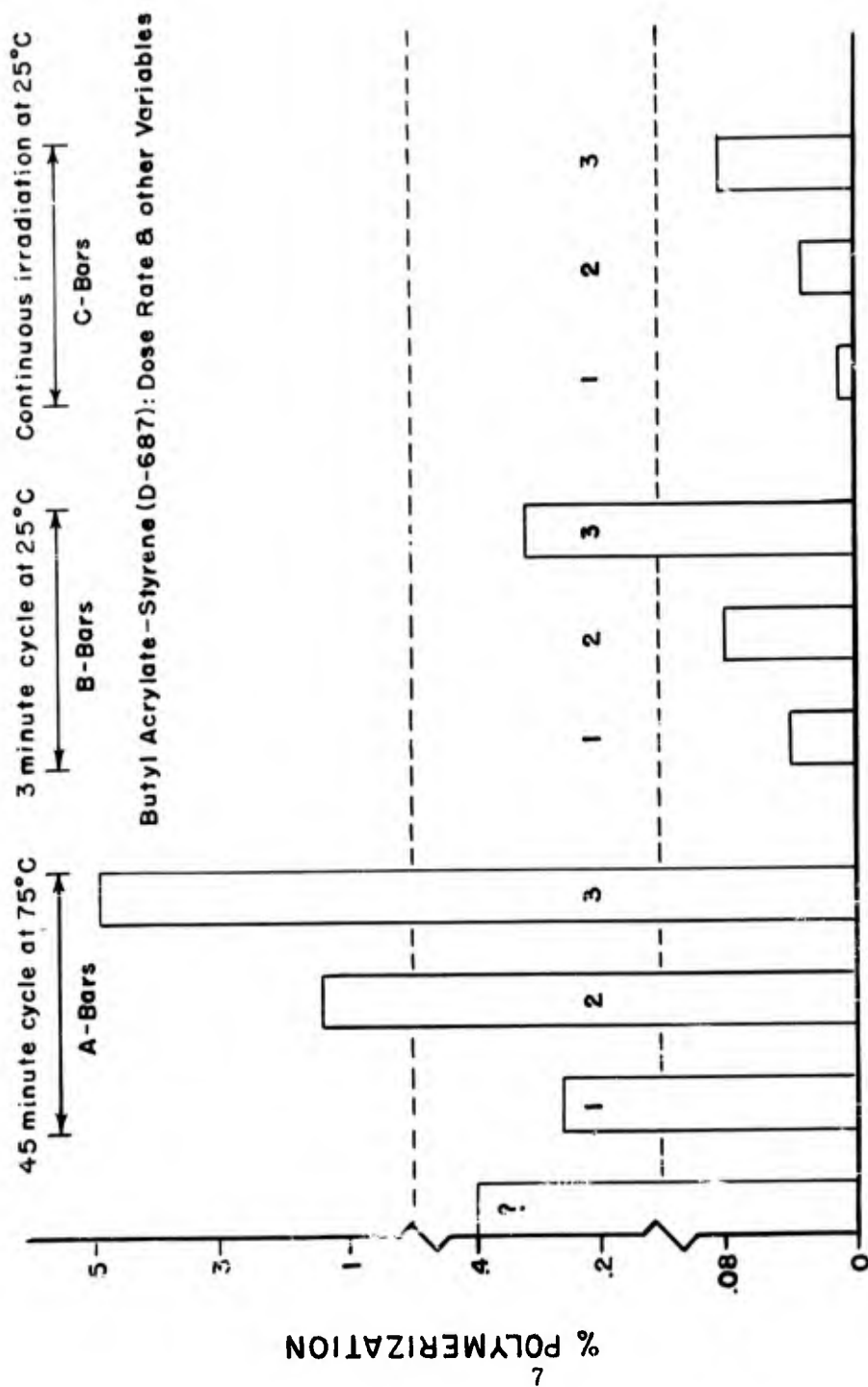
Figure 6. The 1-bars received 1,000 rads per exposure, or 250 rads per second, to a dose of 5,000 rads; the 2-bars received 10,000 rads per exposure, or 2,500 rads per second, to a dose of 50,000 rads; and the 3-bars received 100,000 rads per exposure, or 25,000 rads per second, to a dose of 500,000 rads.
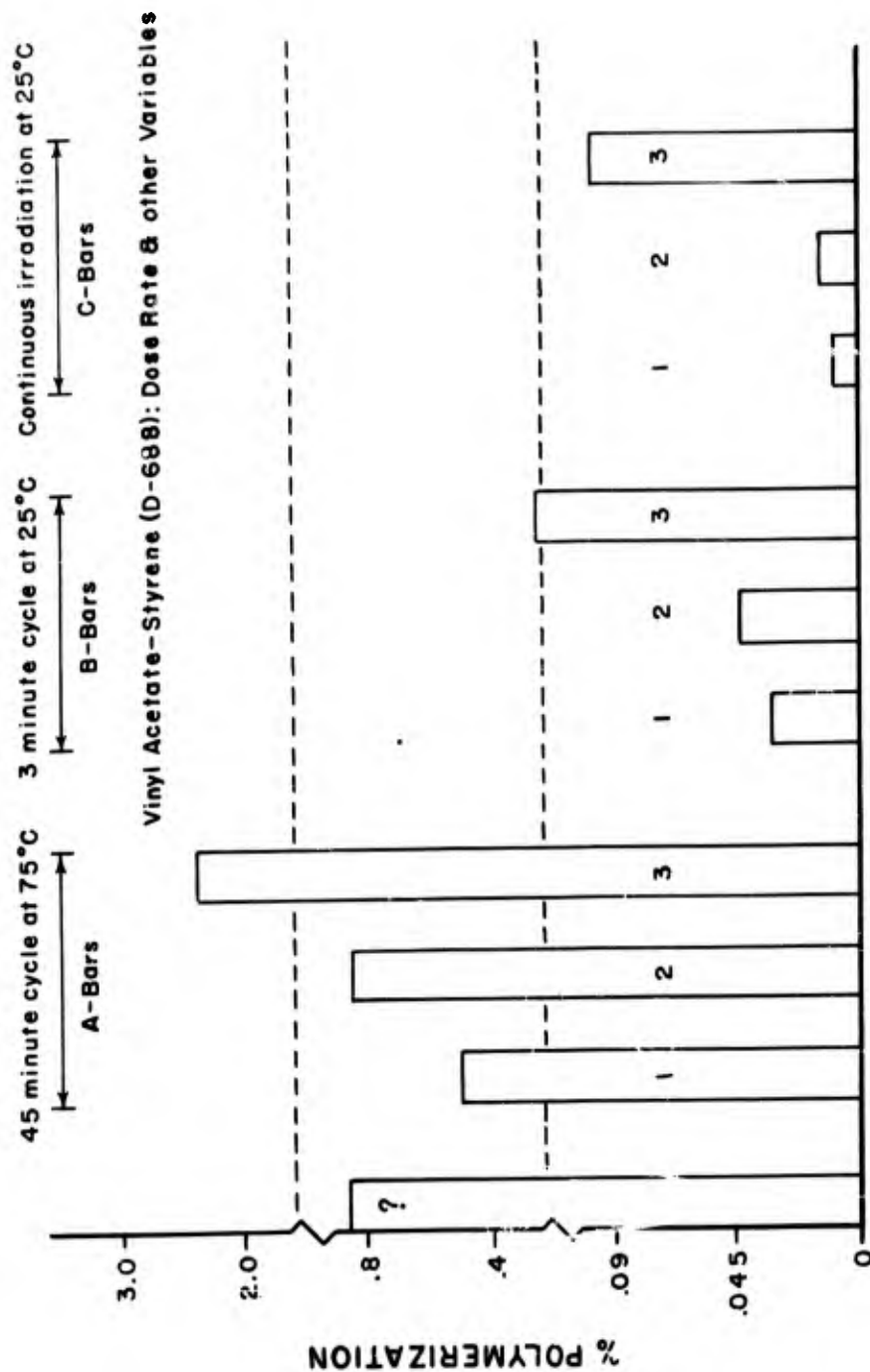
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45 minute cycle at 75°C   3 minute cycle at 25°C   Continuous irradiation at 25°C

A-Bars   B-Bars   C-Bars

Vinyl Acetate-Styrene (D-688): Dose Rate & other Variables

% POLYMERIZATION

3.0   2.0   .8   .4   .09   .045   0

Figure 7. The 1-bars received 1,000 rads per exposure, or 250 rads per second, to a dose of 5,000 rads; the 2-bars received 10,000 rads per exposure, or 2,500 rads per second, to a dose of 50,000 rads; and the 3-bars received 100,000 rads per exposure, or 25,000 rads per second, to a dose of 500,000 rads.

to one degassing, prior to sealing the monomer in the irradiation tubes under diminished pressure. They were then irradiated at three dose rates, and stored at -20°C. until processed.

The results indicated by Figures 8 to 10 were obtained by the addition of 1% of various additives to freshly distilled styrene, which had been dried over anhydrous potassium carbonate, subjected to one degassing before being sealed under reduced pressure in the irradiation tube, and then irradiated at fourteen different dose rates.

The data for the graphs of Figures 11 to 13 (pages 14 to 16) were derived from samples which were not degassed and which were irradiated at nine dose rates in tubes which had not been flamed out.

The results given by Figures 14 to 16 (pages 18 to 20) represent a different version of the data presented by Figures 1 to 6, hence the samples used here were the same as those previously prepared.

The results for Figure 17 (page 22) were obtained from samples which were subjected to one degassing, but those for Figure 18 (page 24) were from samples which were not degassed.

C. Irradiation of Samples

The samples for the data of Figures 1 to 7 were irradiated with a 1.5 Mev electron accelerator operating at 2 Mev for the A- and B-bars and with a 2 Mev resonant transformer for the C-bars, whereas those for Figures 8 to 18 were irradiated with a 1.5 Mev electron accelerator operating at 2 Mev.
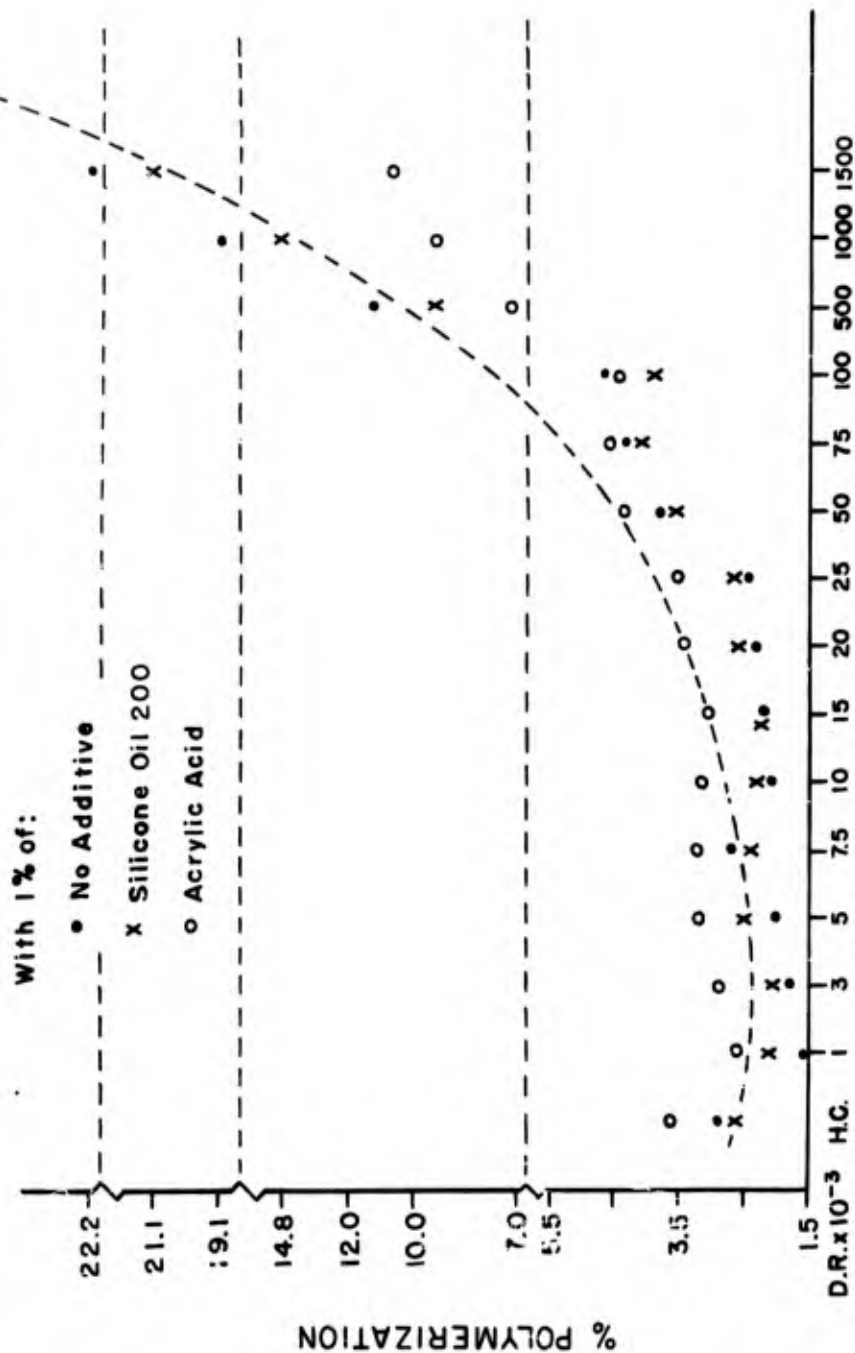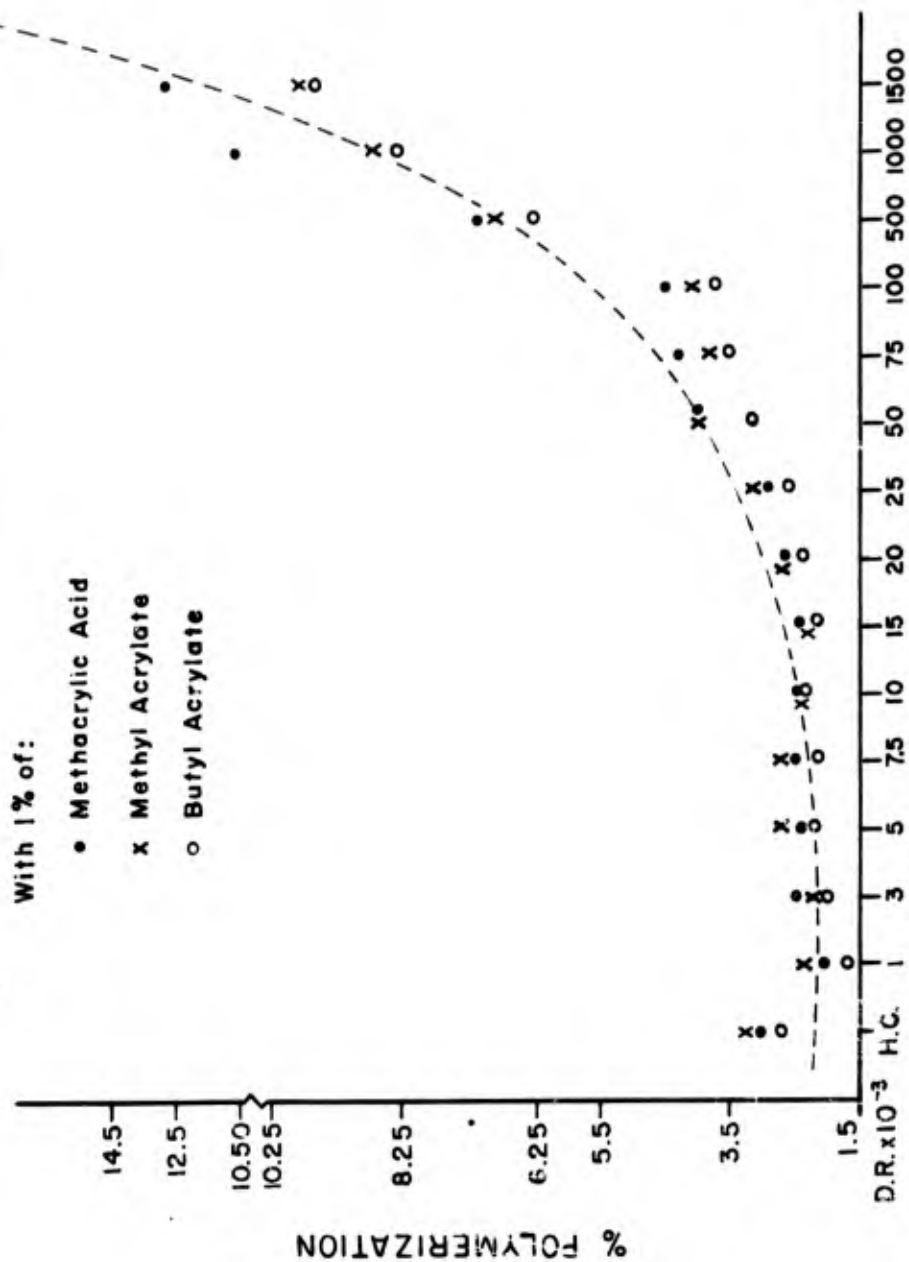
Figure 8. Samples were all degassed once at 7 microns and given five exposures at indicated rates (which should be multiplied by 1,000), on a 45-minute cycle at 75°C. The plotted values are the average from triplicate samples.
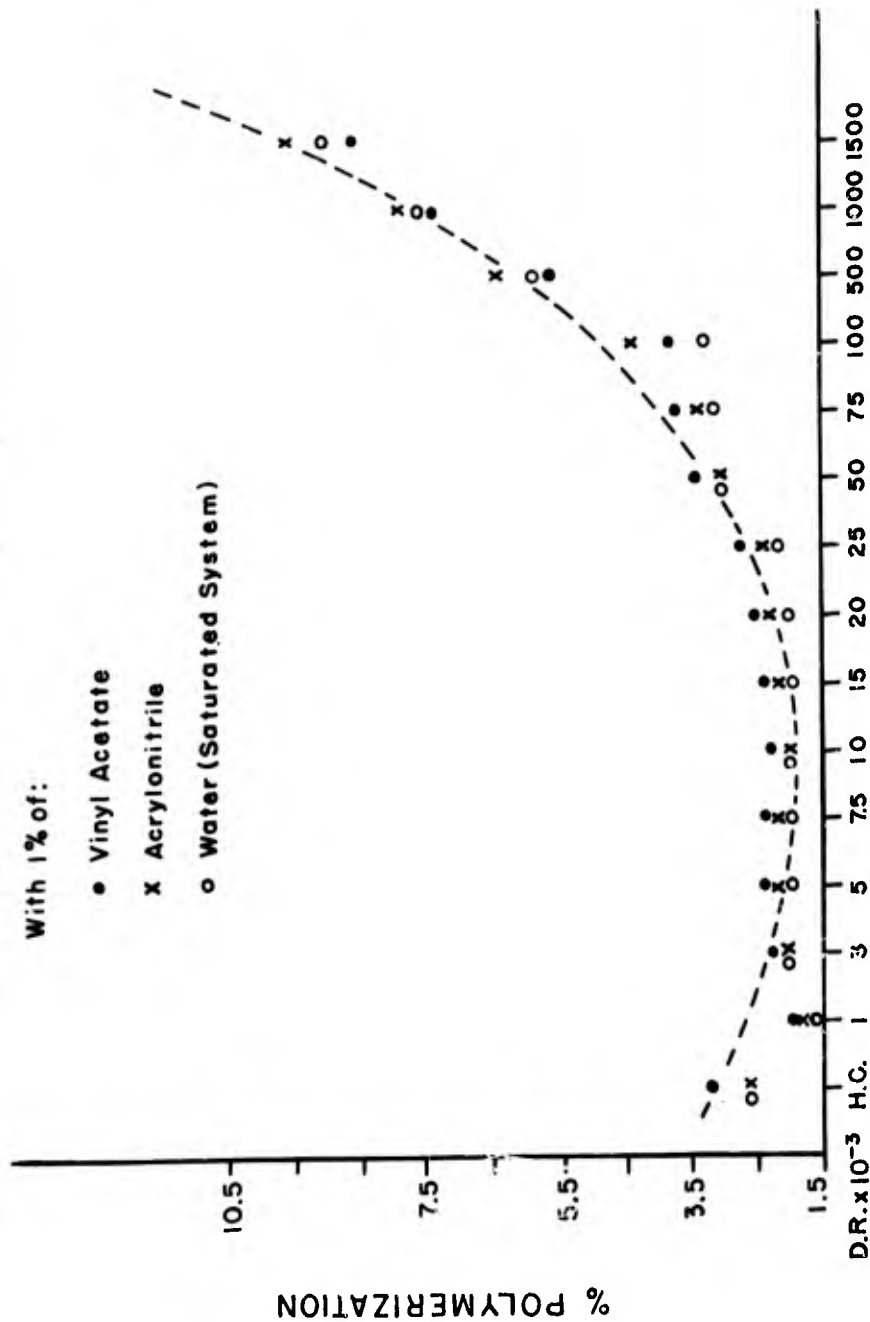
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Figure 9. Samples were all degassed once at 7 microns and given five exposures at indicated rates (which should be multiplied by 1,000), on a 45-minute cycle at 75°C. The plotted values are the average from triplicate samples.

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Figure 10. Samples were all degassed once at 7 microns and given five exposures at indicated rates (which should be multiplied by 1,000), on a 45-minute cycle at ˉ5°C. The plotted values are the average from triplicate samples.

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D. Processing of Samples

The procedure used for the processing of samples was that developed by the Radiation Chemistry Laboratory as recorded in Research Report No. 3, Section D, page 13, November 1960, and in Research Report No. 4, Section D, page 7, December 1960.

E. Experimental Results

In Figures 1 to 7 (pages 2 to 8) the results are presented for seven monomer systems, which were irradiated at three dose rates and dose levels, by use of three irradiation cycles. With the same irradiation cycle, the samples for the No. 2 bars received ten times the dose rate and dose of those for the No. 1 bars, and the samples for the No. 3 bars received in turn ten times the dose rate and dose as did those for the No. 2 bars. If the $kI^{1/2}$ formulation were valid for the conditions of these experiments, the yield represented by the No. 3 bars should be at least ten times those represented by the No. 1 bars. Of the twenty-one comparisons presented (three on each of the seven figures), in the case of the bars for butyl acrylate only does the value for the No. 3 bars approach ten times the comparable value for the No. 1 bars. In the case of butyl acrylate, however, the No. 1 bars represent a total dose of only 1,000 rads whereas the No. 3 bars represent a dose of 500,000 rads. On the basis of these results it must be assumed, therefore, that the $kI^{1/2}$ formulation is not valid for the experimental conditions and operational parameters used in these studies.

The comparable results for the heat control samples are shown at the lower left of the graphs. These are disturbingly high for all of the samples containing styrene, as has been evidenced previously by the heat controls for styrene systems. From the results obtained, one may conclude that flame-out and degassing favor heat-induced polymerization of styrene but do not contribute to the irradiation-induced polymerization of this monomer.
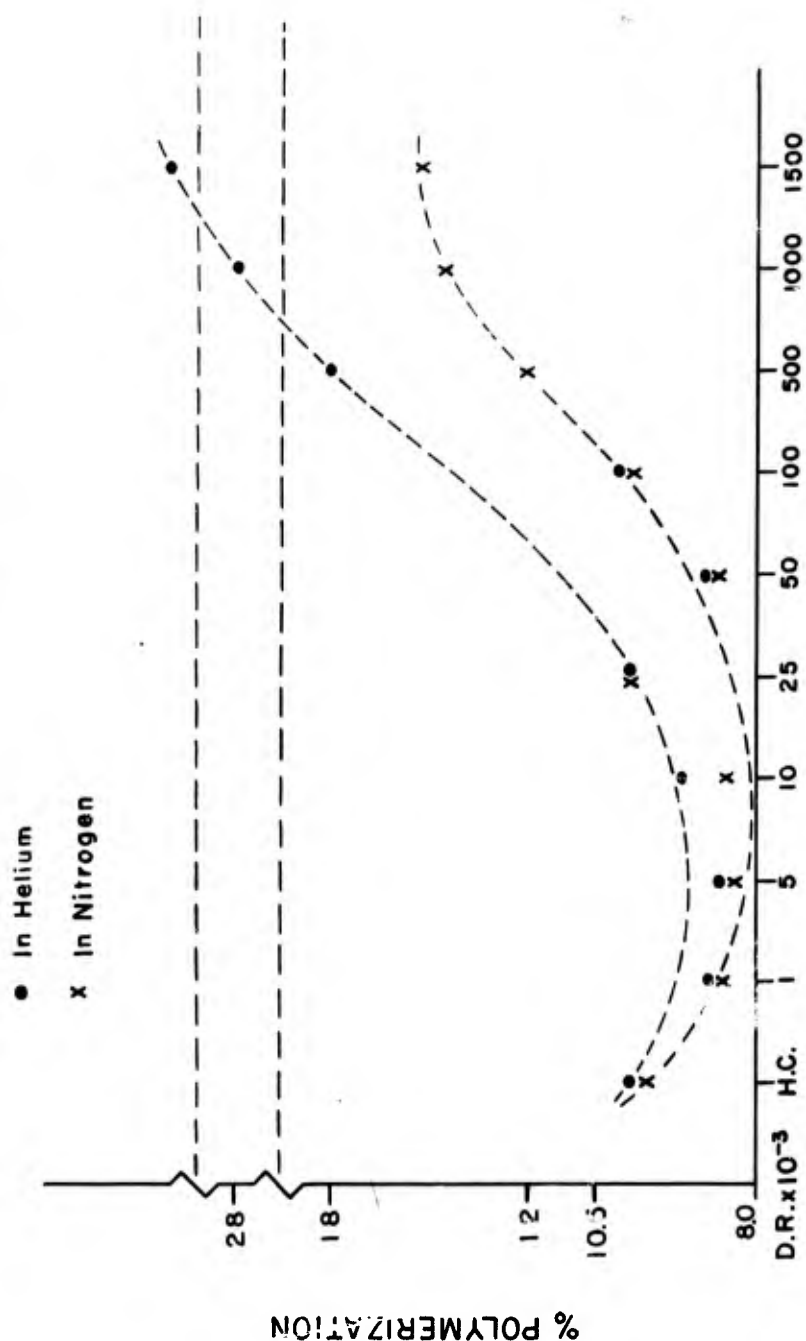
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Figure 11. Samples were given five exposures at the indicated rates (which should be multiplied by 1,000), on a 45-minute cycle at 75°C., with a total heating time of 7.5 hours. The argon and carbon dioxide curves approach the helium curve but the air curve is higher than the helium curve at the lower dose rates. All single determinations. All samples received post-irradiation heating for five days at 50°C.
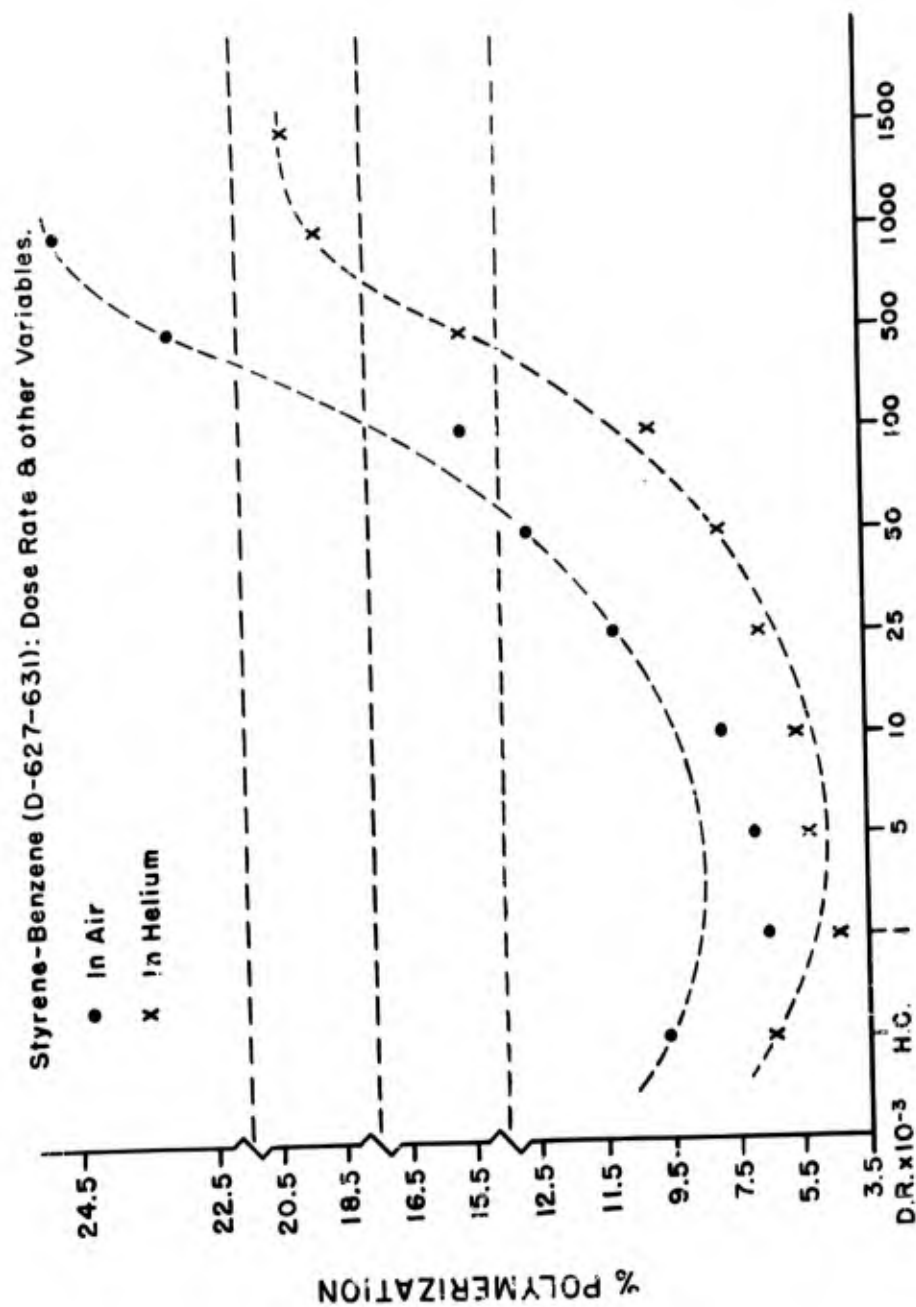
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Figure 12. Samples were given fifteen exposures at the indicated rates, on a 45-minute cycle at 75°C., and a total heating time of 22.5 hours. Styrene-benzene mixture (1:1, v:v). The air, argon, and carbon dioxide curves approach the curve for helium.
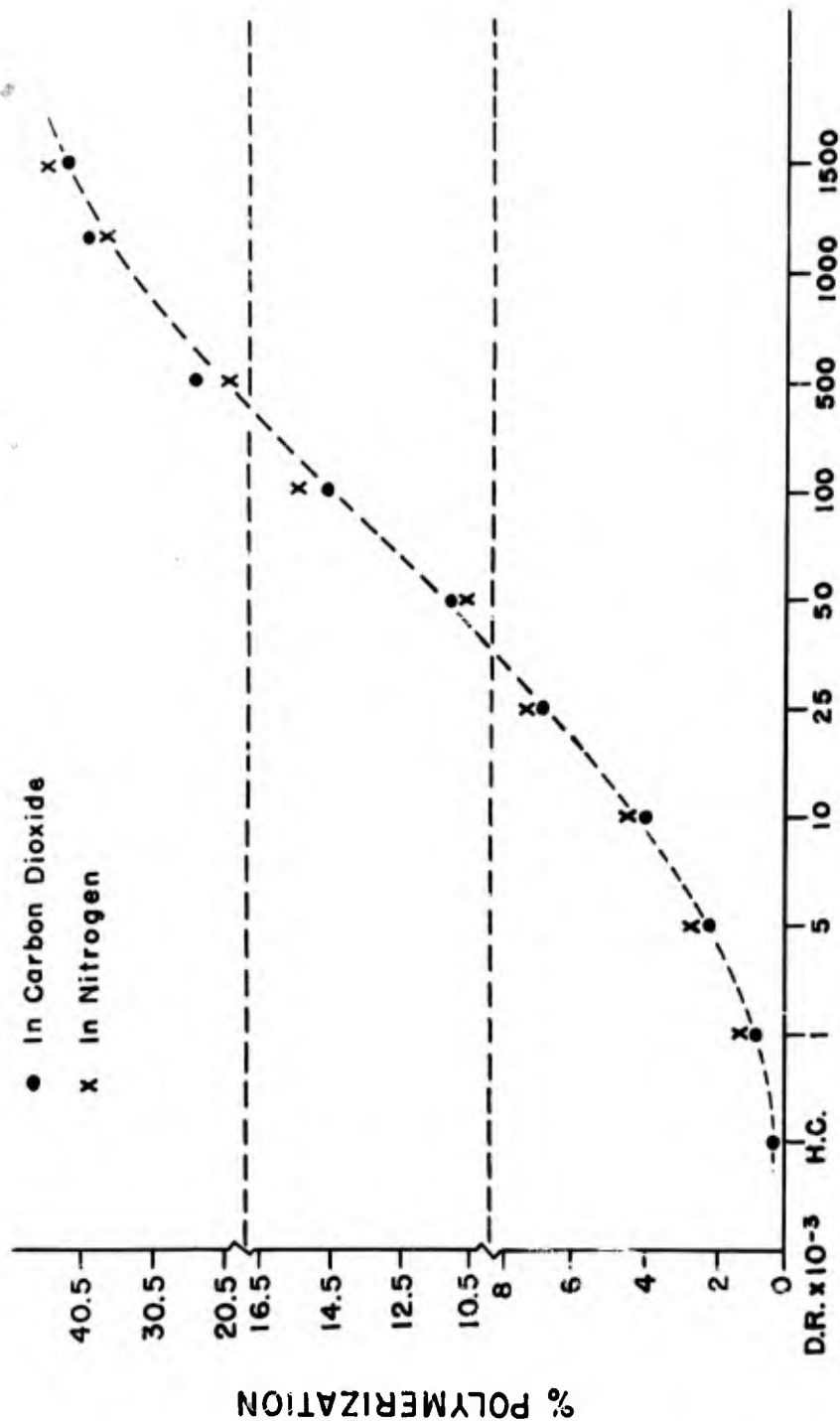
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Figure 13. Samples were given fifteen exposures at the indicated rates, on a 45-minute cycle at 75°C., and a total heating time of 22.5 hours. Vinyl acetate-benzene mixture (1:1, v:v). The air, argon, and helium curves approach the above curve, except for air which is near zero up to 100,000 rads per exposure.

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The results given by Figures 8, 9, and 10 (pages 10 to 12) show the composite effect of fourteen dose rates and nine variations in additives on samples of freshly distilled styrene, which were subjected to one degassing, and irradiated on a forty-five-minute cycle at 75°C. In none of the nine examples cited does the yield of polymer at 100,000 rads per exposure approach ten times that obtained from a dose rate of 1,000 rads per pass for a total dose of 5,000 rads in contrast to a total dose of 500,000 rads at the higher dose rate. It is apparent that the $kI^{1/2}$ formulation does not hold for these experimental conditions and operational parameters. The values for the heat controls, shown by the "H.C." points on these three graphs, indicate in these examples also that the experimental conditions seem to favor heat-induced polymerization much more than they do irradiation-induced polymerization.

Figure 11 (page 14) presents the results obtained from the irradiation-induced polymerization of styrene in five atmospheres and at nine dose rates and dose levels. Only two representative curves, however, are given on the graph. Comparable graphs are given by Figure 12 (page 15) for a one-to-one mixture of benzene and styrene. These samples received fifteen exposures at each of the indicated dose rates. On both of these graphs the values indicated for the heat controls are much higher than comparable samples which were irradiated at low dose rates. Tentatively, this abnormality must be attributed to the apparent fact that the experimental conditions and operational parameters are much more conducive to heat-induced polymerization of styrene than they are to irradiation-induced polymerization.

Data obtained from the irradiation-induced polymerization of a vinyl acetate-benzene mixture (v:v, 1:1) are represented by Figure 13 (page 16). The composite effect of five atmospheres and nine dose rates and dose levels is considered. The air, argon, and helium curves approach those obtained for carbon dioxide and nitrogen except that the curve
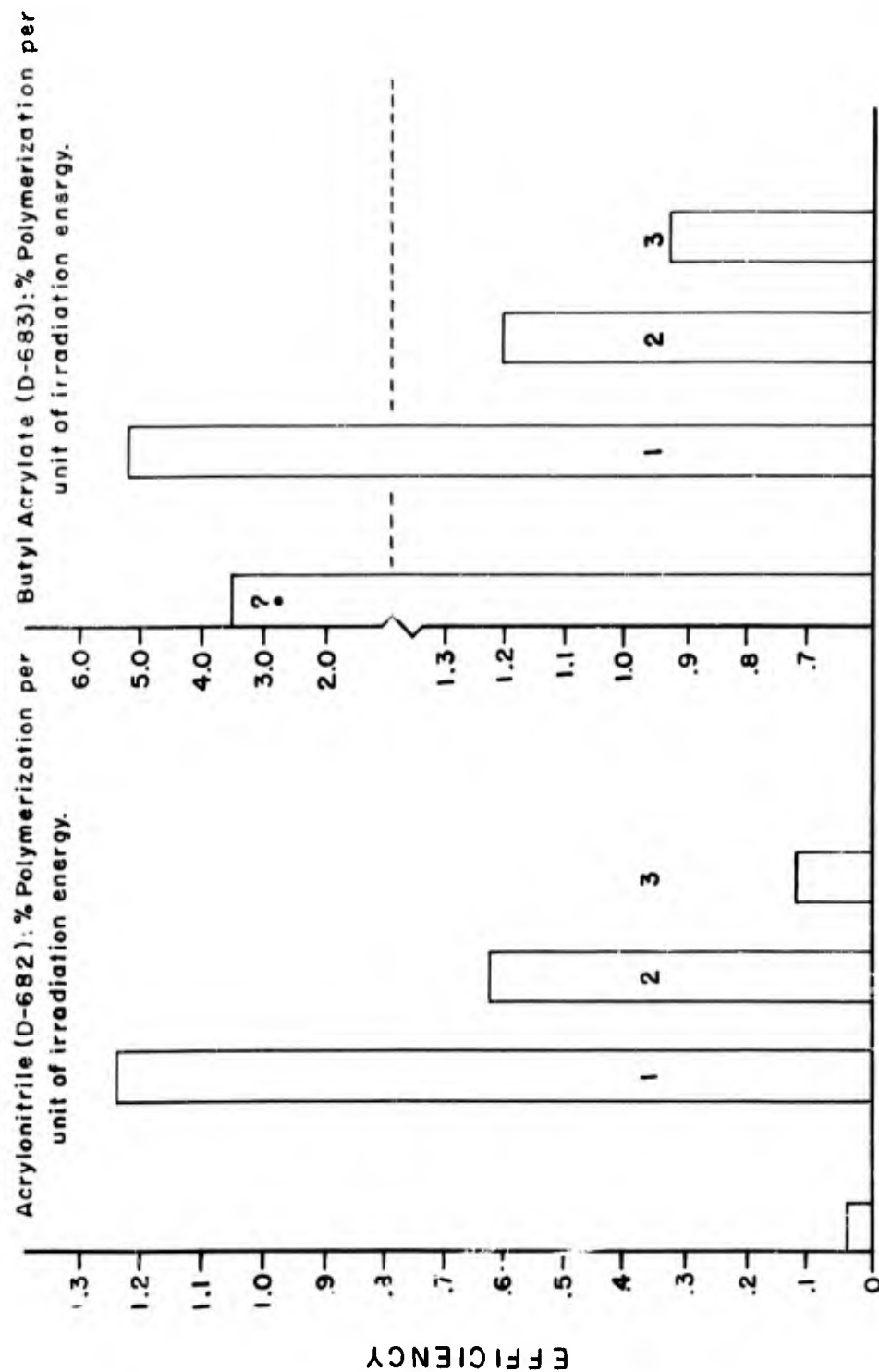
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Figure 14. Data from the **A**-bars of Figures 1 and 2 have been divided by the appropriate number in order to reduce them all to the same total dose of 5,000 rads. This, obviously, is not a fair treatment but it does reduce the system to a single variable, namely, dose rate.
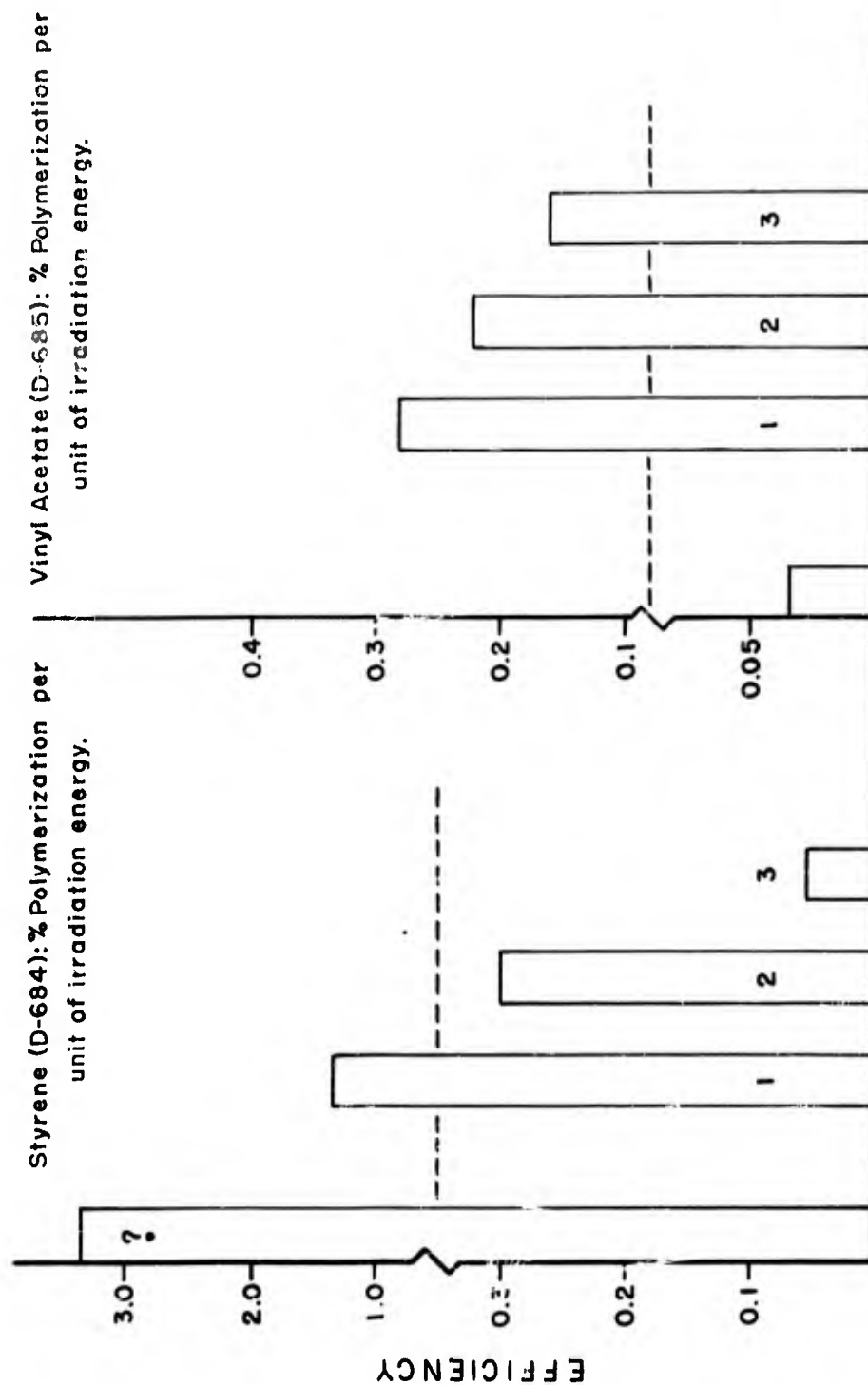
18

Figure 15. Data from the A-bars of Figures 3 and 4 have been divided by the appropriate number to reduce the three bars of each group to the same total dose of 5,000 rads. This, obviously, is not a fair treatment but it does reduce the system to a single variable, namely, dose rate.
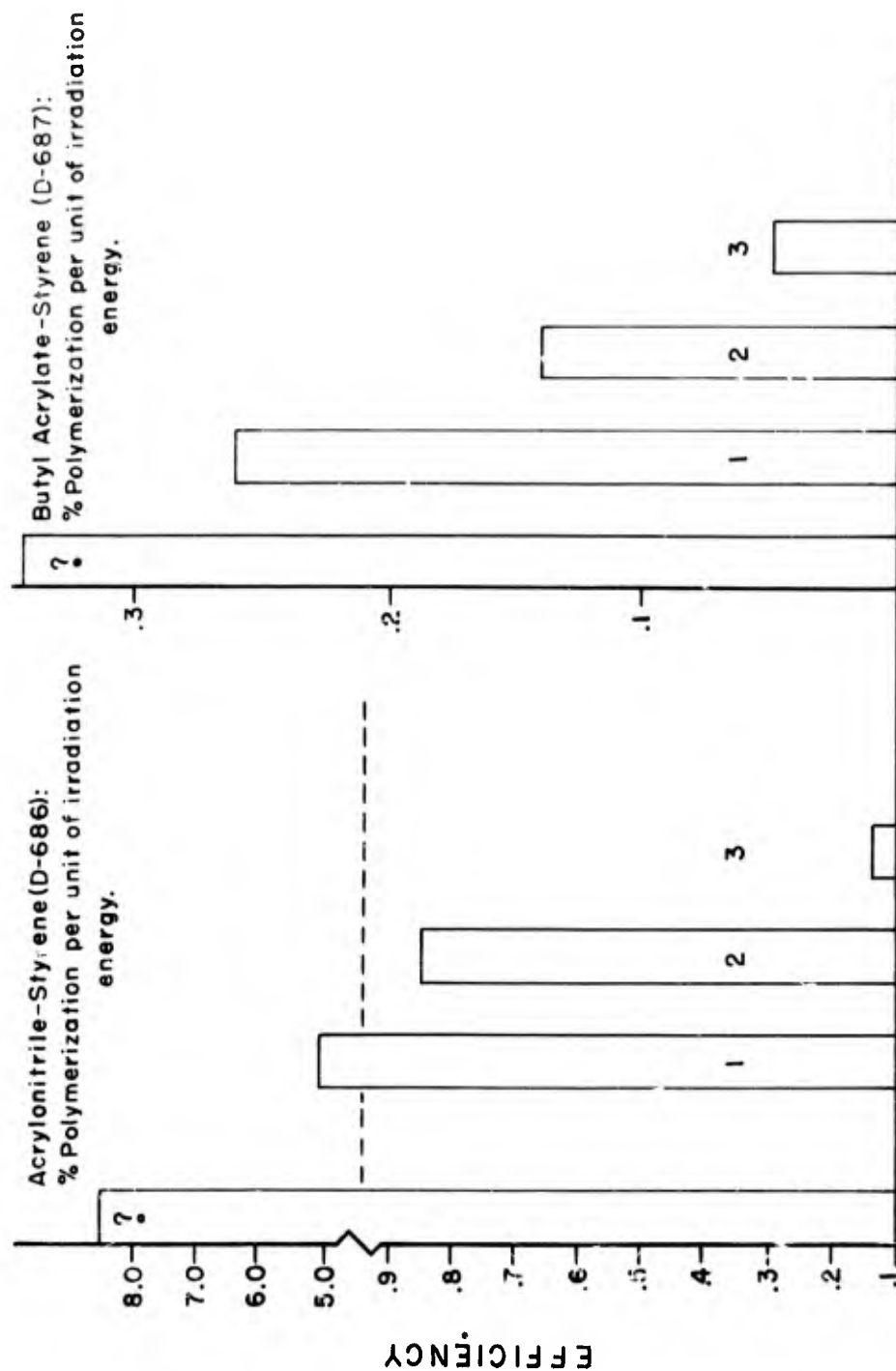
Figure 16. Data from the A-bars of Figures 5 and 6 have been divided by the appropriate number to reduce the three bars of each group to the same total dose of 5,000 rads. This, obviously, is not a fair treatment but it does reduce the system to a single variable, namely, dose rate.

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for air is near zero up to a dose rate of about 100,000 rads per exposure. The heat control, represented by the "H. C." point, does not exhibit the abnormality observed from the heat controls for styrene. The yield from fifteen exposures at 1,000 rads each gave 0.96% polymer whereas that obtained from comparable exposures at 100,000 rads was 14.8%, or approximately 5% more than would be indicated from the $kI^{1/2}$ formulation.

Figures 14, 15, and 16 (pages 18 to 20) present the efficiency (per cent polymerization per unit of radiation energy) graphs for the data of Figures 1 to 6. The values for the No. 1 bars result from a dose rate of 1,000 rads per exposure, those for the No. 2 bars from 10,000 rads per exposure, and those for the No. 3 bars from a dose rate of 100,000 rads per exposure. The general and significant trend is one of increased efficiency or increased polymerization per unit of radiation energy with a decrease in dose rate.

The results from the irradiation-induced polymerization of a butyl acrylate-styrene mixture (1:1, v:v) are given by Figure 17 (page 22), where per cent polymerization is plotted as the ordinate and total dose as the abscissa, with each point from left to right representing both an increase in dose rate and an increase in total dose. Whereas about 0.5% of polymer is obtained at a dose rate of 1,000 rads, only something like 3% is obtained at 100,000 rads per exposure.

The bar graphs of Figure 18 (page 24) record the results obtained from the irradiation-induced polymerization of styrene, vinyl acetate, and acrylonitrile at dose rates of 5,000 and 10,000 rads per exposure and total doses of 25,000 and 50,000 rads. The ratio of the yield of polymer at the higher dose rate to that at the lower dose rate for styrene is 1.2, for vinyl acetate it is 1.6, and for acrylonitrile it is 1.3. To obtain these ratios, however, both twice the dose rate and twice the total dose were used.
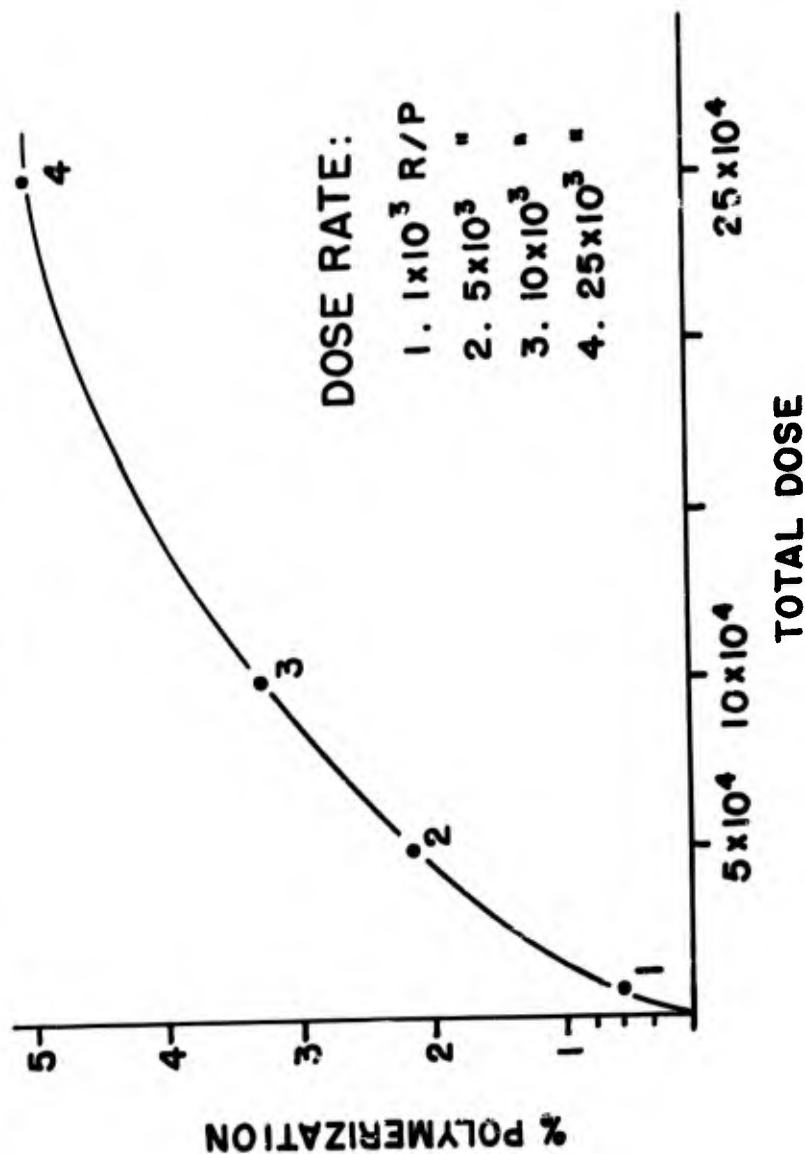
Figure 17. On this graph per cent polymerization is plotted against total dose, but each point on the graph from left to right represents an increase in dose rate as well as an increase in dose. All samples were given one degassing.

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F. Summary

From the results presented by these eighteen graphs one may conclude that the effect of dose rate in the irradiation-induced polymerization of vinyl monomer systems:

    1. Is a function of the monomer system.

    2. Is interdependent on the experimental conditions and operational parameters.

    3. Does not follow the $kI^{1/2}$ formulation for the monomer systems studied under the experimental conditions and operational parameters employed.
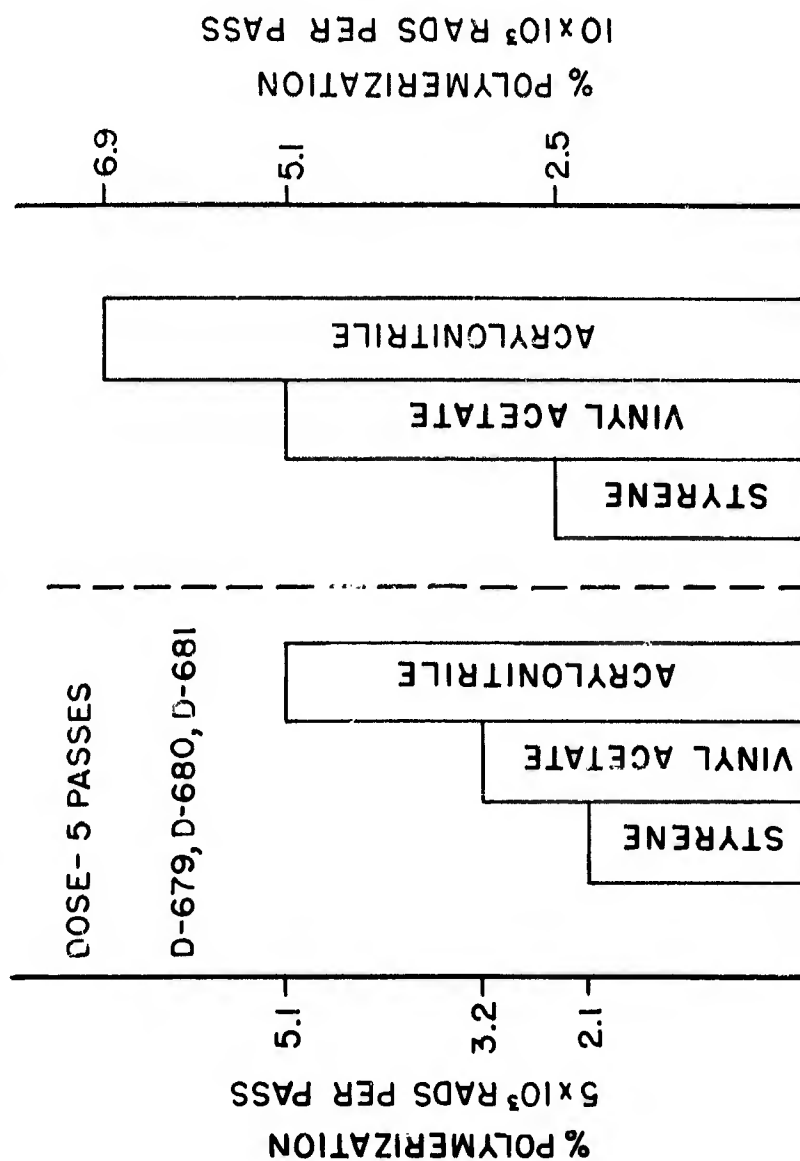
G. Acknowledgments

Figure 18. A comparative study in dose rate, in which the three bar graphs to the right received twice the dose rate and twice the total dose as did those on the left. Styrene, 2.1 vs. 2.5%; vinyl acetate, 3.2 vs. 5.1%; and acrylonitrile, 5.1 vs. 6.9%.